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(54) Title: ION-EXCHANGE MATERIALS

(57) Abstract: An ion-exchange material, for example a polymer electrolyte membrane or gas diffusion electrode comprises a semi-crystalline copolymer comprising: a first unit which includes an ion-exchange site; a second crystalline unit; and a third unit which is amorphous. The third unit is used to disrupt the crystallinity of the copolymer thereby to increase its solubility in solvents. The material described may be used in fuel cells.

ION-EXCHANGE MATERIALS

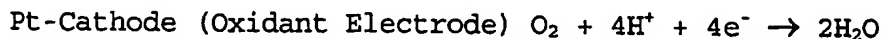
This invention relates to an ion-exchange materials (e.g. polymer electrolyte membranes) and particularly, although not exclusively, relates to a method of preparing an ion-exchange membrane and such a membrane per se.

One type of polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:



Thus, electrons and protons are consumed to produce water and heat. Connecting the two electrodes through an

external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

Preferred ion-conducting polymeric materials for use
5 as components of polymer electrolyte membranes in fuel cells have high conductivity (low EW, or high ion-exchange capacities), low water uptake, robustness and solubility in solvents which can be used to cast the membranes. However, some of the aforementioned requirements compete
10 with one another. For example, steps taken to increase solubility of the materials in casting solvents may, disadvantageously, increase the water uptake of the materials; and steps taken to increase the conductivity of the materials will tend also to increase water absorption
15 leading to premature failure of the materials when used in fuel cells.

It is an object of the present invention to address problems associated with the provision of polymer
20 electrolyte membranes and/or gas diffusion electrodes.

The invention is based on the appreciation that copolymers comprising crystallisable units may be robust and provide membranes of low water absorption.
25 Nonetheless, it has been appreciated that whilst the solubility of such copolymers in polar aprotic solvents (e.g. NMP) used to cast the membranes can be very low, the solubility can be increased by including a moiety in the copolymer which disrupts the crystallinity of the
30 crystallisable unit, thereby reducing the crystallinity of the polymer. Nevertheless, whilst the crystallinity is reduced so that the copolymers have an increased solubility in polar aprotic solvents, the robustness and

solubility in water are not significantly detrimentally affected.

According to a first aspect of the invention, there is
5 provided a polymer electrolyte membrane or a gas diffusion electrode which include a semi-crystalline copolymer comprising:

- a first unit which includes an ion-exchange site;
- 10 a second crystalline unit; and
- a third unit which is amorphous.

The existence and/or extent of crystallinity in a polymer may be measured by wide angle X-ray diffraction
15 (also referred to as Wide Angle X-ray Scattering or WAXS), for example as described by Blundell and Osborn (Polymer 24, 953, 1983). Details are provided in Example 8c hereinafter. Alternatively, crystallinity may be assessed by Differential Scanning Calorimetry (DSC).

20

The level of crystallinity (or "Crystallinity Index") of said semi-crystalline copolymer, suitably measured as described above, may be at least 0.5%, is preferably at least 1%, is more preferably at least 3% and, especially
25 is at least 5%. In some cases, the crystallinity may be greater than 10% or even greater than 12%. The crystallinity may be less than 20% or less than 15%.

Suitably, "A*" represents the mole% of said first unit
30 in said copolymer; "B*" represents the mole % of said second unit; and "C*" represents the mole % of said third unit.

Suitably, A* is at least 15, preferably at least 20, more preferably at least 25, especially at least 30. It may be less than 70, preferably less than 60, more preferably less than 50. Preferably, A* is in the range
5 25-60.

B* may be at least 5. Suitably, B* is at least 15, preferably at least 25, more preferably at least 30, especially at least 35. It may be less than 70, preferably
10 less than 60, more preferably less than 55. Preferably, B* is in the range 5-70.

Suitably, C* is at least 5, preferably at least 7.5, preferably at least 10, especially at least 12.5. In some
15 cases C* may be at least 25. C* may be less than 70, preferably less than 60, more preferably less than 55. In other cases, C* may be less than 30, preferably less than 25, more preferably less than 20, especially 15 or less. Preferably, C* is in the range 5 to 70.

20

Said copolymer is preferably non-fluorinated.

Said first unit is preferably a repeat unit which suitably includes aromatic group containing moieties
25 linked by -SO₂- and/or -CO- and/or -Q- groups, where Q is O or S. Because said first unit includes ion-exchange sites, for example, sulphonate groups, it will not be crystalline, but will be amorphous.

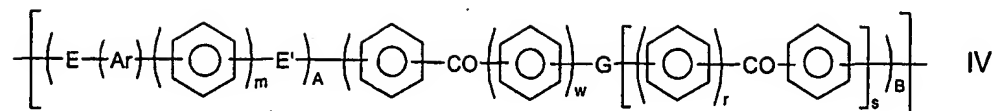
30 Said second unit is preferably a repeat unit which suitably includes aromatic group containing moieties linked by -CO- and/or -Q- groups, where Q is as described

above. The second unit preferably does not include $\text{-SO}_2\text{-}$ groups since such would tend to render the unit amorphous.

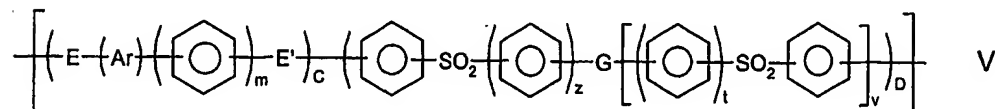
Said third unit is preferably a repeat unit which
5 suitably includes aromatic group containing moieties
linked by $\text{-SO}_2\text{-}$ and/or -CO- and/or -Q- groups, where Q is
as described above provided, however, that said third unit
suitably includes a means to render it amorphous
(hereinafter said "amorphous means") and/or not
10 crystallisable with polyarylether ketones or
polyarylthioether ketones and/or not crystallisable with
the second unit described above.

Said third unit may comprise a fourth unit which is of
15 formula -Q-Z-Q- wherein Z represents said aromatic group
containing moiety, wherein said fourth unit is not
symmetrical about an imaginary line which passes through
the two -Q- moieties provided, however, that said fourth
unit is not derived from dihydroxybenzophenone substituted
20 by groups Q at the 4- and 4'- positions (since such a
benzophenone acts in the manner of a symmetrical moiety by
virtue of the carbonyl group being substantially similar
to an ether group thereby allowing the carbonyl group to
be interchanged with an ether group in a
25 polyaryletherketone crystal lattice). Said third unit,
for example moiety Z, may include a bulky group.

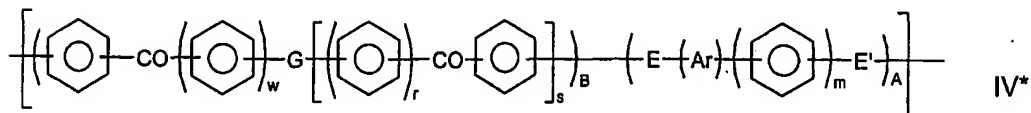
Said semi-crystalline copolymer may include a first
unit which is of general formula



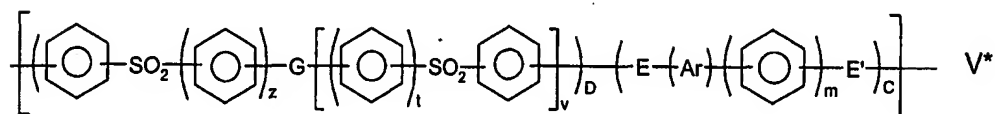
or of general formula



5 or of general formula



or of general formula

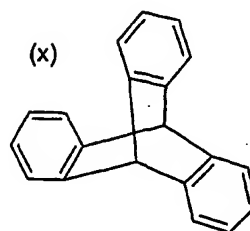
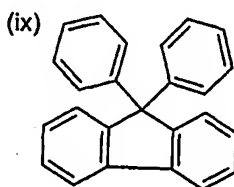
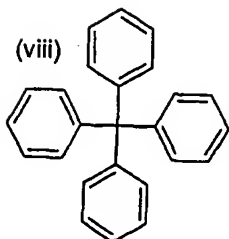
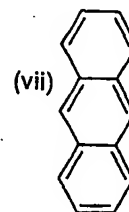
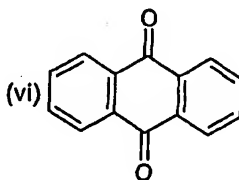
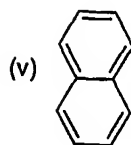
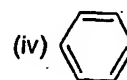
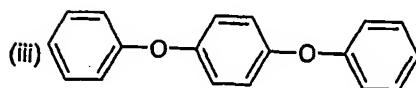
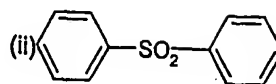
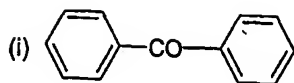
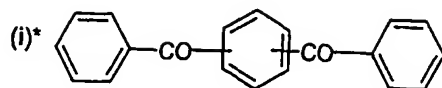


10

wherein said first unit is functionalised to provide ion-exchange sites; wherein the phenyl moieties in units IV, IV*, V and V* are independently optionally substituted wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)* and (i) to (x) which is

15

bonded via one or more of its phenyl moieties to adjacent moieties



5 In (i)*, the middle phenyl may be 1,4- or 1,3-substituted.

Suitably, to provide said ion exchange sites, said
 copolymer is sulphonated, phosphorylated, carboxylated,
 10 quaternary-aminoalkylated or chloromethylated, and

optionally further modified to yield $-\text{CH}_2\text{PO}_3\text{H}_2$, $-\text{CH}_2\text{NR}_3^{20+}$ where R^{20} is an alkyl, or $-\text{CH}_2\text{NAr}_3^{x+}$ where Ar^x is an aromatic (arene), to provide a cation or anion exchange membrane. Further still, the aromatic moiety may contain a hydroxyl group which can be readily elaborated by existing methods to generate $-\text{OSO}_3\text{H}$ and $-\text{OPO}_3\text{H}_2$ cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

10 Preferably, said first unit is sulphonated. Preferably, the only ion-exchange sites of the first unit are sites which are sulphonated.

References to sulphonation include a reference to substitution with a group $-\text{SO}_3\text{M}$ wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR_4^{Y+} , in which R^Y stands for H, $\text{C}_1\text{-C}_4$ alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H, NR_4^+ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

Where a phenyl moiety described herein is optionally substituted, it may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred alkyl groups are C_{1-10} , especially C_{1-4} , alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic

groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

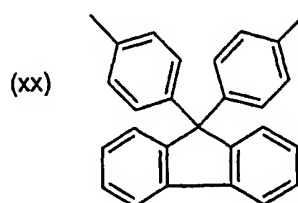
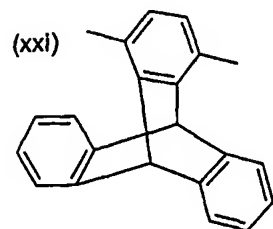
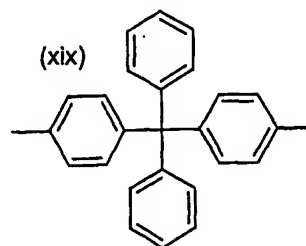
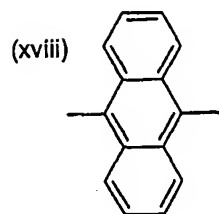
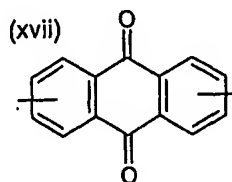
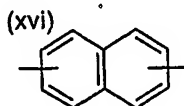
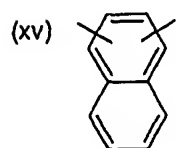
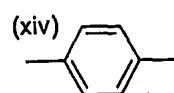
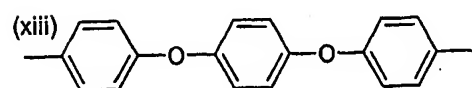
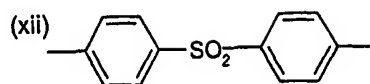
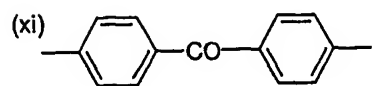
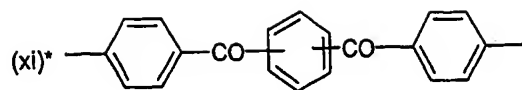
Another group of optional substituents of a phenyl moiety comprises alkyls, halogens, C_yF_{2y+1} where y is an integer greater than zero, $O-R^q$ (where R^q is selected from the group consisting of alkyls, perfluoralkyls and aryls), $CF=CF_2$, CN , NO_2 and OH . Trifluormethylated phenyl moieties may be preferred in some circumstances.

Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene moieties have 1,4- linkages.

Preferably, the polymeric chain of the copolymer does not include a -S- moiety. Preferably, G represents a direct link.

Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1

Preferably Ar is selected from the following moieties (xi)* and (xi) to (xxi):



In (ix)*, the middle phenyl may be 1,4- or 1,3-substituted.

5 Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

10 A preferred first unit includes an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be sulphonated under relatively mild conditions to
15 introduce two sulphonate groups per unit. Thus, preferred polymers may have at least 10π electrons in a delocalized aromatic moiety. The number of π electrons may be 12 or less. Preferred polymers include a biphenylene moiety. Other preferred polymers include a naphthalene moiety.
20 Preferred polymers include said electron rich, non-deactivated, easily sulphonatable unit bonded to two oxygen atoms. Especially preferred polymers include a -O-biphenylene-O- moiety. Other especially preferred polymers include a -O-naphthalene-O- moiety.

25 Preferred first units include a first type of moiety which is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the
30 relatively mild method described in Example 7 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 7 may be advantageous over currently used methods

which use oleum. A preferred second said moiety includes a moiety $-\text{Ph}_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen. Especially preferred is the case wherein said moiety is $-\text{O}-\text{Ph}_n-\text{O}-$ where said ether groups are para to the Ph-Ph bond.

Said semi-crystalline polymer may include a second crystalline unit which is of general formula IV or IV* as described above, provided said unit is crystallisable. Suitably, to be crystallisable, said second unit does not include any Ar group of formula (ii), (viii), (ix) or (x). More preferably, it may also not include an Ar group of formula (v), (vi) or (vii). Preferred Ar groups consist of one or more phenyl groups in combination with one or more carbonyl and/or ether groups.

Said semi-crystalline polymer may include a third unit which is of general formula IV, IV*, V or V*, provided, however, that said unit includes at least some moieties whose shape and/or conformation is/are incompatible with the crystalline conformation of said second crystalline unit so that said third unit is amorphous. Preferably, said third unit includes an $-\text{SO}_2-$ moiety; a bulky group or a moiety which is not symmetrical as described above.

25

Preferred first units may be -ether-phenyl-ketone-phenyl, -ether-phenyl-ketone-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl, -ether-biphenyl-ether-phenyl-ketone-phenyl, ether-phenyl-ether-phenyl-ketone-phenyl, ether-naphthalene-ether-phenyl-ketone-phenyl, ether-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl, -ether-diphenyl-ether-phenyl-sulphone-phenyl- and -ether-phenyl-ether-phenyl-sulphone-phenyl, suitably functionalised with ion-

exchange sites. Another preferred first unit is ether-phenyl-sulphone-phenyl. Preferred second units may be ether-phenyl-ketone-phenyl-ketone-phenyl-, ether-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl-, ether-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl-, ether-phenyl-ketone-phenyl-, ether-phenyl-ketone-phenyl-, ether-phenyl-ketone-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl and ether-biphenyl-ether-phenyl-ketone-phenyl-. Preferred third units may be ether-phenyl-sulphone-phenyl and ether-phenyl-ether-phenyl-sulphone-phenyl. Another preferred third unit may be a - 1,3-dioxy-4-(phenylcarbonyl) phenyl moiety derived from 2,4-DHB as herein defined.

In said copolymer, the mole% of co-monomer units, for example said first, second and third repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

Preferred polymers suitably have a solubility of at least 4% w/w in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated. However, in some situations it may be possible to effect bi- or multi-sulphonation.

In general terms, where a said copolymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a copolymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl

moieties may be sulphonated. It is believed to be possible to sulphonate relatively easily $-O-(\text{phenyl})_n-O-$ moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula $-O-(\text{phenyl})_n-CO-$ or $-O-(\text{phenyl})_n-SO_2-$ may also be sulphonated at up to 100 mole% but more vigorous conditions may be required. Moieties of formulae $-CO-(\text{phenyl})_n-CO-$ and $-SO_2-(\text{phenyl})_n-SO_2-$ are more difficult to sulphonate and may be sulphonated to a level less than 100 mole% or not at all under some sulphonation conditions.

10

The glass transition temperature (T_g) of said copolymer may be at least 144°C , suitably at least 150°C , preferably at least 154°C , more preferably at least 160°C , especially at least 164°C . In some cases, the T_g may be at least 170°C , or at least 190°C or greater than 250°C or even 300°C .

Said copolymer may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm^{-3} , said solution containing 1g of polymer per 100cm^3 of solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm^{-3} , said solution containing 0.1g of polymer per 100cm^3 of solution.

The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

The main peak of the melting endotherm (T_m) for said polymer (if crystalline) may be at least 300°C.

In general terms, said polymer is preferably
5 substantially stable when used as a PEM in a fuel cell.
Thus, it suitably has high resistance to oxidation,
reduction and hydrolysis and has very low permeability to
reactants in the fuel cell. Preferably, however, it has a
high proton conductivity. Furthermore, it suitably has
10 high mechanical strength and is capable of being bonded to
other components which make up a membrane electrode
assembly.

Said polymer may comprise a film, suitably having a
15 thickness of less than 1mm, preferably less than 0.5mm,
more preferably less than 0.1mm, especially less than 0.05
mm. The film may have a thickness of at least 5 μ m.

Said polymer electrolyte membrane may comprise one or
20 more layers wherein, suitably, at least one layer comprises
a film of said polymer. Said membrane may have a thickness
of at least 5 μ m and, suitably, less than 1mm, preferably
less than 0.5mm, more preferably less than 0.1mm,
especially less than 0.05mm.

25

The polymer electrolyte membrane may be a composite
membrane which may include a support material for the semi-
crystalline copolymer for importing mechanical strength and
dimensional stability to the membrane. The copolymer may
30 be associated with the support material to form a composite
membrane in a variety of ways. For example, an unsupported
conductive polymer film of the copolymer can be preformed
and laminated to the support material. Alternatively, (and

preferably) the support material may be porous and a solution of the copolymer can be impregnated into the support material. In one embodiment, the support material may comprise, or preferably consist essentially of, polytetrafluoroethylene, suitably provided as a porous film. Such a support material may be as described and used in accordance with the teachings of WO97/25369 and WO96/28242, the contents of which are incorporated herein by reference. Suitably, the support material has a porous microstructure of polymeric fibrils and is impregnated with said copolymer throughout the material, preferably so as to render an interior volume of the membrane substantially occlusive.

15 In another embodiment, a porous support material may be provided by a fabric, for example of polyetheretherketone, which may have warp and weft strands or may comprise an irregular arrangement of fibres. Suitably, said pores are defined by the void volume of the fabric - that is between the fibres. However, the fibres of the fabric themselves may be porous and penetrated by said conductive polymer. Alternatively, a said porous support material may be microporous and may suitably be made by a phase inversion process. Such a microporous material preferably has no through pores and/or contains no closed pores. Further details on the porous support materials described may be found in PCT/GB00/03449, the contents of which are incorporated herein by reference.

30 In a further embodiment, said support material may comprise a conductive polymer as described in GB0006880.9, the contents of which are incorporated herein by

reference. For example, said support material may comprise an ion-conducting microporous membrane.

Said semi-crystalline copolymer could be a component of
5 a blend of polymers. In such a blend, said semi-crystalline copolymer preferably comprises at least 80%, more preferably at least 90wt% thereof. Preferably, however, said semi-crystalline copolymer is not a component of a blend.

10

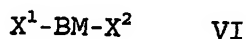
The polymer electrolyte membrane suitably includes a layer of a catalyst material, which may be a platinum catalyst (i.e. platinum containing) or a mixture of platinum and ruthenium, on both sides of the polymer film.
15 Electrodes may be provided outside the catalyst material.

According to a second aspect of the invention, there is provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane
20 according to the first aspect.

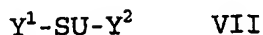
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According to a third aspect of the invention, there is provided any novel polymer as described according to said first aspect per se.

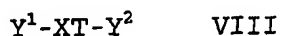
According to a fourth aspect of the invention, there is provided a process for the preparation of a semi-crystalline polymer described in the first, second or third aspects, the process comprising polycondensing a compound
30 of formula



with a compound of formula

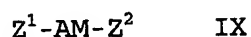


5 and with a compound of formula



and with a compound of formula

10



thereby to prepare a copolymer, wherein Y^1 represents a halogen atom or a group -EH (or -E'H if appropriate) and X^1 represents the other one of a halogen atom or group -EH (or -E'H if appropriate), Y^2 represents a halogen atom or a group -E'H and X^2 represents the other one of a halogen atom or a group -E'H (or -EH if appropriate) and Z^1 and Z^2 represent a halogen atom or a group -EH (or E'H if appropriate);

and wherein BM represents part of a base monomer, SU represents part of a moiety which is functionalised or can be functionalised (suitably independently of other moieties in the copolymer) to provide ion-exchange sites, XT represents a part of a crystalline or crystallisable moiety and AM represents part of an amorphous moiety.

The polycondensation reaction described is suitably carried out in the presence of a base, especially an alkali metal carbonate or bicarbonate or a mixture of such bases. Preferred bases for use in the reaction include

sodium carbonate and potassium carbonate and mixtures of these.

The identity and/or properties of the polymers
5 prepared in a polycondensation reaction described may be varied according to the reaction profile, the identity of the base used, the temperature of the polymerisation, the solvent(s) used and the time of the polymerisation. Also, the molecular weight of a polymer prepared controlled by
10 using an excess of halogen or hydroxy reactants, the excess being, for example, in the range 0.1 to 5.0 mole%

In a polymer prepared in a said polycondensation reaction involving compounds of general formula VI, VII,
15 VIII and IX, moieties of general formula VI, VII, VIII and IX (excluding end groups Y^1 , Y^2 , X^1 , X^2 , Z^1 and Z^2) may be present in regular succession (that is, with single units of one said moiety, separated by single units of another said moiety or moieties), or semi-regular succession (that
20 is, with single units of one said moiety separated by strings of another moiety or moieties which are not all of the same length) or in irregular succession (that is, with at least some multiple units of one moiety separated by strings of other moieties that may or may not be of equal
25 lengths). The moieties described are suitably linked through ether or thioether groups.

Also, moieties in compounds VI, VII, VIII, and/or IX arranged between a pair of spaced apart -O- atoms and
30 which include a -phenyl-SO₂ or -phenyl-CO- bonded to one of the -O- atoms may, in the polymer formed in the polycondensation reaction, be present in regular

succession, semi-regular succession or in irregular succession, as described previously.

In any sampled polymer, the chains that make up the polymer may be equal or may differ in regularity from one another, either as a result of synthesis conditions or of deliberate blending of separately made batches of polymer.

In a first embodiment, where Z^1 and Z^2 in compound IX are the same as Y^1 and Y^2 respectively in other compounds used, the polycondensation of compounds VI, VII, VIII and IX may result in the preparation of a copolymer which includes units of formula

-BM-Q-SU-Q- X

-BM-Q-XT-Q- XI and

-BM-Q-AM-Q- XII

20

where Q is as described above.

In a second embodiment, where Z^1 and Z^2 in compound IX and X^1 and X^2 in compound VI are either all halogens (which may be all the same or the halogens may be different e.g. Z^1 and Z^2 could both be chlorine and X^1 and X^2 could both be fluorine) or all comprise a group -EH (or E^1H if appropriate), the polycondensation may result in the preparation of a copolymer which includes units of formula

30

-BM-Q-SU-Q- XX

-BM-Q-XT-Q- XXI

-XT-Q-AM-Q- XXII and

-SU-Q-AM-Q- XXIII

where Q is as described above.

5 In a third embodiment, a polycondensation may use two different compounds of formula IX. In one of the compounds Z^1 and Z^2 may be as described according to the first embodiment and in the other Z^1 and Z^2 may be as described according to the second embodiment and, therefore, a
10 copolymer which includes units of formulae X, XI, XII, XXII XXIII and a unit -AM-Q-AM-Q- (where the AM moieties are the same or different) may be formed.

 Whilst the moiety SU of monomer VII could be
15 functionalised to provide ion-exchange sites, functionalisation is preferably undertaken after monomers VII and VI have been reacted, and suitably after said copolymer has been prepared. If, however, the moiety SU of monomer VII is sulphonated and then polymerized, there may
20 be no need to sulphonate the copolymer formed. In this case, XT may include moieties which would sulphonate (e.g. easy to sulphate units such as biphenyl) if the copolymer itself was sulphonated.

25 Preferably, ion-exchange sites are provided by sulphonation.

 Sulphonation as described herein may be carried out in concentrated sulphuric acid (suitably at least 96% w/w,
30 preferably at least 97%w/w, more preferably at least 98%w/w; and preferably less than 98.5%w/w) at an elevated temperature. For example, dried copolymer may be contacted with sulphuric acid and heated with stirring at a

temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours, more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled
5 water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

Suitably, "a*" represents the mole% of compound VI used
10 in the process; "b*" represents the mole % of compound VII used in the process; "c*" represents the mole % of compound VIII used in the process; and "d*" represents the mole% of compound IX used in the process.

15 When copolymers of formulae X, XI and XII are prepared in the process, as described in said first embodiment, preferably, a* is in the range 45-55, especially 48-52; and the sum of b*, c* and d* is in the range 45-55, especially 48-52.

20

Where copolymers of formulae XX, XXI, XXII and XXIII are prepared in the process, as described in said second embodiment, the sum of a* and d* is preferably in the range 45-52, especially 48-52; and the sum of b* and c* is
25 preferably in the range 45-52, especially 48-52.

Where different compounds of formula IX are used, as described in the third embodiment, the sum of the mole% of the halogen-containing components is preferably in the
30 range 45-52, especially 48-52; and the sum of the mole% of the -EH (or -E¹H if appropriate) - containing components is preferably in the range 45-52, especially 48-52.

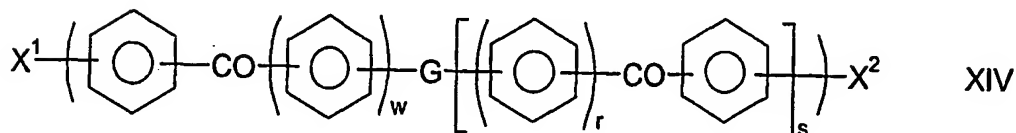
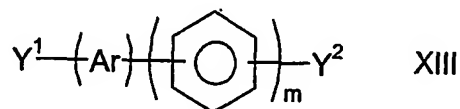
Where copolymers of formula X, XI and XII are prepared, preferably b^* is in the range 10-30; preferably, c^* is in the range 2.5 to 40; ; and preferably, d^* is in the range 2.5 to 40, . d^* may be up to 100%, suitably up to 95%,
 5 preferably up to 90%, more preferably up to 85%, especially up to 80% of the sum of $c^* + d^*$.

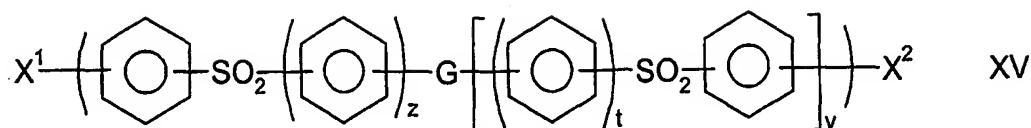
In some cases, d^* may be less than 30%, preferably less than 20%, more preferably less than 15%, especially less
 10 than 10% of the sum of c^* and d^* .

Where copolymers of formulae XX, XXI, XXII and XXIII are prepared in the process, a^* may be in the range 25-52, especially 30-52; d^* is in the range 2.5-40, especially 5-
 15 20; b^* is in the range 12.5-30, and c^* is in the range 2.5 to 40

The sum of a^* , b^* , c^* and d^* is suitably 100.

20 BM, SU and AM may independently be represented by any of the following formulae

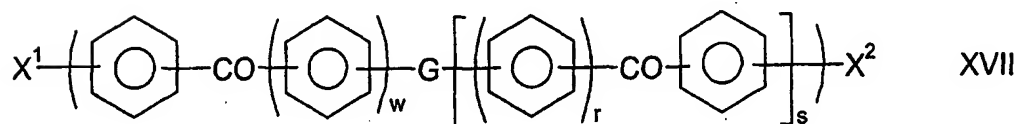
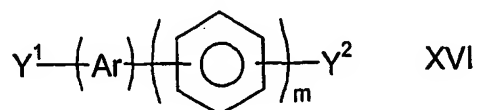




wherein Ar, m, w, r, s, z, t, v and G are as described in any statement herein.

XT may be represented by one of the following formulae

5



10 provided the unit is crystallisable as described above with respect to the selection of the second unit of formula IV or IV*.

In some situations, the polymer prepared, more
15 particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after polymer formation.

Preferred halogen atoms are fluorine and chlorine
20 atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to activating groups, especially carbonyl groups.

The molecular weight of the copolymer can be controlled by using an excess of halogen or hydroxy reactants. The excess may typically be in the range 0.1 to 5.0 mole %. The polymerisation reaction may be terminated by addition
5 of one or more monofunctional reactants as end-cappers.

The invention extends to a method of manufacturing a device selected from a fuel cell, electrolyser or gas diffusion electrode, the method including the step of using
10 a semi-crystalline copolymer to prepare an ion-conducting element of the device.

The device is preferably a fuel cell and the element is preferably a polymer electrolyte membrane thereof.
15

Sulphonated polymers described herein may be made into films and/or membranes for use as PEMs by conventional techniques, for example as described in Examples 5 to 7 of US 5561202.
20

Advantageously, sulphonated polymers may be dissolved in a solvent used to cast a film and/or membrane at relatively high temperature, for example at a temperature of greater than 100°C, preferably greater than 120°C, more
25 preferably greater than 140°C, especially greater than 145°C. The use of relatively high temperatures may facilitate the manufacture of films.

Thus, the invention extends to method of making a film
30 and/or a membrane, suitably for a fuel cell or electrolyser or any other use described herein, the method comprising contacting a polymer which includes ion-exchange sites (and is preferably a sulphonated polymer, especially as

described herein) with a solvent wherein the temperature of the solvent is greater than 100°C, preferably greater than 120°C, more preferably greater than 140°C, especially greater than 145°C, whereby the polymer dissolves in the solvent and subsequently casting the solvent with dissolved polymer to make said film and/or membrane.

The sulphonated polymers described herein may be used as polymer electrolyte membranes in fuel cells or electrolyzers as described. Additionally, they may be used in gas diffusion electrodes. The following further utilities for the membranes are also contemplated:

1. Proton exchange membrane based water electrolysis, which involves a reverse chemical reaction to that employed in hydrogen/oxygen electrochemical fuel cells.
2. Chloralkali electrolysis, typically involving the electrolysis of a brine solution to produce chlorine and sodium hydroxide, with hydrogen as a by-product.
3. Electrode separators in conventional batteries due to the chemical inertness and high electrical conductivity of the composite membranes.
4. Ion-selective electrodes, particularly those used for the potentiometric determination of a specific ion such as Ca^{2+} , Na^+ , K^+ and like ions. The composite membrane could also be employed as the sensor material for humidity sensors, as the electrical conductivity of an ion exchange membrane varies with humidity.
5. Ion-exchange material for separations by ion-exchange chromatography. Typical such applications are deionization and desalination of water (for example, the purification of heavy metal contaminated water), ion separations (for example, rare-earth metal ions,

trans-uranium elements), and the removal of interfering ionic species.

6. Ion-exchange membranes employed in analytical preconcentration techniques (Donnan Dialysis). This technique is typically employed in analytical chemical processes to concentrate dilute ionic species to be analysed.
7. Ion-exchange membranes in electrodialysis, in which membranes are employed to separate components of an ionic solution under the driving force of an electrical current. Electrolysis applications include the industrial-scale desalination of brackish water, preparation of boiler feed make-up and chemical process water, de-ashing of sugar solutions, deacidification of citrus juices, separation of amino acids, and the like.
8. Membranes in dialysis applications, in which solutes diffuse from one side of the membrane (the feed side) to the other side according to their concentration gradient. Separation between solutes is obtained as a result of differences in diffusion rates across the membrane arising from differences in molecular size. Such applications include hemodialysis (artificial kidneys) and the removal of alcohol from beer.
9. Membranes in gas separation (gas permeation) and pervaporation (liquid permeation) techniques.
10. Bipolar membranes employed in water splitting and subsequently in the recovery of acids and bases from waste water solutions.

Any feature of any aspect of any invention or example described herein may be combined with any feature of any aspect of any other invention or example described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte fuel cell.

5

The following abbreviations are used hereinafter

BP - 4,4'-dihydroxybiphenyl

DHB - 4,4'-dihydroxybenzophenone

10

Bis-S - 4,4'-dihydroxydiphenylsulphone

2,4-DHB is 2,4-dihydroxybenzophenone

BDF - 4,4'-difluorobenzophenone

15

Unless otherwise stated, all chemicals referred to hereinafter were used as received from Sigma-Aldrich Chemical Company, Dorset, U.K.

20

As described above, the fuel cell includes a thin sheet 2 of a hydrogen conducting Polymer Electrolyte Membrane.

The polymers for Polymer Electrolyte Membranes in accordance with embodiments of the invention are copolymers which include a first repeat unit which comprises a
25 sulphonated polyarylether ketone
(polyetherdiphenyletherketone). Because the unit is sulphonated, it will not be crystalline. In some cases, the first unit may be etherdiphenylethersulphone. The polymers include a second repeat unit which is crystalline.
30 It includes ether and ketone units separated by phenyl groups. The ketone units can be interchanged with ether units in a crystal lattice so the polyetherketone units described are crystalline. The greater the extent of the

polyaryetherketone chains, the greater the crystallinity of the copolymer. A third unit is included in the copolymer which is provided to reduce the level of crystallinity in the copolymer. The third unit includes units which cannot
5 interchange with ether units in the crystal lattice and, therefore, disrupt the crystallinity of the second units.

In the following examples, Examples 1 and 4 are comparative examples. Example 1 describes the preparation
10 of a copolymer using a mole ratio of BP:DHB of 1:1. Examples 2 and 3 show the effect of substituting some of the DHB with Bis-S. Example 4 describes the preparation of a copolymer using a mole ratio of BP:DHB of 1:2. Examples
5 and 6 show the effect of substituting some of the DHB with Bis-S and 2,4'-DHB respectively. Example 9a describes the preparation of a copolymer where the ratio of BP:
15 (DHB+Bis-S) is 1:1.5 and the ratio of DHB:BIS-S is 40:60. Examples 9b-f describe the preparation of a copolymer where the ratio of BP:(DHB+Bis-S) is 1:1.5 and the ratio of
20 DHB:Bis-S is varied.

Example 1 (comparative)

A 700 flanged flask fitted with a ground glass
25 Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (37.24g, 0.20 mole)
4,4'-dihydroxybenzophenone (42.84g, 0.20 mole), and diphenylsulphone (332g) and purged with nitrogen for over 1
30 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was

added. The temperature was raised gradually to 330°C over 3 hours then maintained for 1 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.48 kNsm⁻².

Example 2

10

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (37.24g, 0.20 mole), 4,4'-dihydroxydiphenylsulphone (10.01g, 0.04 mole), 4,4'-dihydroxybenzophenone (34.28, 0.16 mole) and diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 320°C over 3 hours then maintained for 1.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.34 kNsm⁻².

30 Example 3

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and

outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (37.24g, 0.20 mole), 4,4'-dihydroxydiphenylsulphone (15.02g, 0.06 mole), 4,4'-dihydroxybenzophenone (29.99g, 0.14 mole) and
5 diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was
10 added. The temperature was raised gradually to 320°C over 3 hours then maintained for 1 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was
15 dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.42 kNsm⁻².

Example 4

20 A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (24.83g, 0.133 mole) 4,4'-dihydroxybenzophenone (57.41g, 0.268 mole), and
25 diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was
30 added. The temperature was raised gradually to 330°C over 3 hours then maintained for 1 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.54 kNsm⁻².

5

Example 5a

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and
10 outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (. 24.83g, 0.133 mole), 4,4'-dihydroxydiphenylsulphone (13.35g, 0.053 mole), 4,4'-dihydroxybenzophenone (45.7g, 0.213 mole) and diphenylsulphone (332g) and purged with nitrogen for over 1
15 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 320°C over
20 3 hours then maintained for 1.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt
25 viscosity at 400°C, 1000sec⁻¹ of 0.37 kNsm⁻².

Examples 5b-5e and 5f(comparative)

The polymerisation procedure of Example 5a was
30 followed, for 5b-5e, except that copolymers were prepared by varying the mole ratios of the hydroxy-containing reactants. The polymerisation procedure for 5f is described below.

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (24.83g, 0.133 mole) 4,4'-dihydroxydiphenylsulphone (66.73g, 0.267 mole), and diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (42.44g, 0.4 mole) and potassium carbonate (1.11g, 0.008 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.62 kNsm⁻².

A summary of the mole ratios and MVs are detailed in the Table below. Example 5f is an amorphous equivalent of the other polymers.

Example	Polymer composition (mole ratio)				MV (kNsm ⁻²)
	BDF	BP	DHB	Bis-S	
5a	1.02	0.33	0.536	0.133	0.37
5b	1.02	0.33	0.402	0.268	0.47
5c	1.02	0.33	0.335	0.335	0.48
5d	1.02	0.33	0.268	0.402	0.48
5e	1.02	0.33	0.133	0.536	0.53
5f	1.02	0.33	-	0.67	0.62

Example 6a

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole) 4,4'-dihydroxybiphenyl (24.83g, 0.133 mole), 2,4-dihydroxybenzophenone (11.42g, 0.053 mole), 4,4'-dihydroxybenzophenone (45.7g, 0.213 mole) and diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 320°C over 3 hours then maintained for 1.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.80 kNsm⁻².

Example 6b

The polymerisation procedure of Example 6a was followed except that a copolymer was prepared with a different mole ratio of the hydroxy-containing reactants. A summary of the mole ratios and MVs for Examples 6a and 6b are detailed in the Table below.

Example	Polymer Composition (mole ratio)				MV (kNsm ⁻²)
	BDF	BP	4,4'-DHB	2,4-DHB	
6a	1.02	0.33	0.533	0.133	0.70
6b	1.02	0.33	0.402	0.268	0.38

Example 7 (General Sulphonation Procedure)

5 The polymers of Examples 1-6 were sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated
10 as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, titration confirmed that 100 mole% of the biphenyl units had sulphonated, giving one sulphonic acid group, ortho to the
15 ether linkage, on each of the two aromatic rings comprising the biphenyl unit.

Example 8a (Membrane Fabrication)

20 Membranes were produced from the polymers from Examples 1 to 6 after sulphonation as described in Example 7 by dissolving respective polymers in N-methylpyrrolidone (NMP). The polymers were dissolved at 80°C at their maximum concentration as shown in the Table below. In one
25 example, a 50:50 w/w blend of the polymers described in Examples 5d and 5e, sulphonated as described in Example 7, was used to prepare a membrane.

The homogeneous solutions were cast onto clean glass plates and then drawn down to give 400 micron films, using a Gardner Knife. The solvent was then evaporated at 100°C under vacuum for 24 hours.

5

Example 8b (Boiling water uptake)

The following general procedure was followed to determine the Boiling Water Uptake.

10

5cm x 5cm x 50 microns samples of membranes were separately immersed in boiling deionised water (500ml) for 60 mins, removed and dried quickly with lint-free paper to remove surface water, weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly. The % water-uptake was calculated as described below:

15

$$\% \text{ Water-uptake} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

20

Results for membranes assessed are provided in the table below.

Sulphonated polymer from Example*	Theoretical EW	Measured EW (by titration)	Concentration in NMP (%w/w)	Boiling Water Uptake (%)
1	458	472	4	237
2	462	483	7.5	300
3	464		10	320
4	654	674	Insoluble	-
5a	657	670	5	69
5b	663	667	7.5	77
5c	670	671	7.5	81
5d	676	685	10	90
5e	683	660	15	172
5f	690	663	15	165
6a	647	666	5	73
6b	655	671	10	100
50:50 w/w blend of polymers from Examples 5d and 5e	680		15	128

* It should be appreciated that the polymers of the referenced Examples are sulphonated as described in Example 7.

It will be noted from the above Table that Example 1 has relatively low solubility in NMP and this is believed to be due to the crystallinity caused by the PEK units in the copolymer. It will, however, be noted from Examples 2 and 3 that the inclusion of Bis-S reduces the crystallinity. This is believed to be due to the fact that Bis-S has a shape and/or conformation which is incompatible with the crystalline regions of the copolymer

(ie the PEK unit) and, accordingly, it disrupts the PEK chains, thereby lowering crystallinity. However, the level of water absorption may not be detrimentally increased. As the level of Bis-S is increased, the level of crystallinity is reduced further (compare Examples 2 and 3). Examples 4 to 6 may be interpreted as for Examples 1 to 3.

Example 8c Determination of the Crystallinity Index values of Sulphonated Polymers from Examples 5b, 5d and 5f by Wide Angle X-Ray Scattering (WAXS)

Crystallinity can be quantified, in one method, by defining a "crystallinity index" for measurements made by Wide Angle X-ray Scattering (WAXS). This approach defines the measurement in relation to the WAXS pattern. The measured area of crystalline peaks in the WAXS pattern is taken as a percentage of the total crystalline and amorphous scatter over a chosen angular range of the pattern. Crystallinity index should, to a first approximation, be proportional to crystallinity for broadly similar polymer materials. It is constrained to be zero when crystallinity is zero and 100% when crystallinity is 100%.

Membranes of the sulphonated polymers from Examples 5b, 5d and 5f as prepared in Example 8a were examined by WAXS as described below.

The membranes were analysed using a Siemens D5000 X-ray diffractometer with Cu K-alpha radiation and a Kevex energy dispersive detector. Measurements were made from a single membrane sheet mounted in symmetrical reflection

geometry. A programmable divergence slit was used to maintain a constant irradiated region of the specimen surface 6 mm long over a 2-theta measurement range of 10 - 49°.

5

The WAXS pattern of the membrane from Example 5f exhibited only broad amorphous scatter, whereas the patterns of the membranes from Examples 5b and 5d exhibited sharper, crystalline peaks in addition to
10 amorphous bands. The intensity of the bands for Example 5b was greater than for Example 5d.

The measured WAXS patterns were analysed by first making a background correction, subtracting the
15 corresponding WAXS pattern from a blank specimen holder. The resulting patterns were fitted by a combination of a pattern measured from a similar but amorphous membrane film and a set of peaks (at approximately 18.8, 20.8, 22.9, 29.1 and 40.0 ° 2-theta) corresponding to those
20 observed in the more crystalline membranes. The crystallinity index was calculated as the total area fitted by these peaks taken as a percentage of the combined area of the fitted peaks and the fitted amorphous pattern.

25

The results are detailed in the Table below.

Sulphonated polymer from Example	Crystallinity Index (%)
5f	0
5d	2.1
5b	7.1

Example 9a

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (29.79g, 0.16 mole), 4,4'-dihydroxydiphenylsulphone (36.04g, 0.144 mole), 4,4'-dihydroxybenzophenone (20.57g, 0.096 mole) and diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 320°C over 3 hours then maintained for 1.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.6 kNsm⁻².

Example 9b - 9e and 9f (comparative)

The polymerisation procedure of Example 9a was followed, except that copolymers were prepared by varying the mole ratios of the hydroxy-containing reactants. A summary of the mole ratios and the MVs are detailed in the Table below.

Example	Polymer composition (mole ratio)				MV (kNsm ⁻²)
	BDF	BP	DHB	Bis-S	
9a	1.02	0.4	0.24	0.36	0.6
9b	1.02	0.4	0.36	0.24	0.21
9c	1.02	0.4	0.39	0.21	0.32
9d	1.02	0.4	0.42	0.18	0.44
9e	1.02	0.4	0.6	-	0.45
9f	1.02	0.4	-	0.6	0.26

Example 10a Sulphonation and subsequent dissolution of Polymer from Example 9a

5 The polymer from Example 9a was sulphonated as described in Example 7 and dissolved in NMP at 15 %w/w at two different temperatures, 80° and 150°C. The sulphonated polymers from both thermal treatments were completely soluble producing homogeneous solutions, 10 filtered through a 10 micron filter, cast on to clean glass plates and drawn down to give 400 micron films, using a Gardner Knife. The solvent was evaporated at 100°C under vacuum for 24 hours.

15 The effect of the two thermal treatments on the sulphonated polymer was investigated by evaluating the following:

20 Reduced Viscosity (RV):

measured at 25°C on a solution of the polymer in NMP, the solution containing 1g of polymer/100cm³ of solution.

Gel Permeation Chromatography (GPC):

Triple Detector GPC using DMSO
as the solvent with the
addition of 0.05% lithium
chloride

5

Ion Exchange Capacity (IEC): titration

Boiling Water Uptake: as described in Example 8b

Test	Sulphonated Polymer dissolved at 80°C	Sulphonated Polymer dissolved at 150°C
RV	1.22	1.22
GPC Mn	28700	24800
Mw	47600	47000
PDI	1.7	1.9
Ion Exchange Capacity (meq/g)	1.72	1.72
Boiling Water Uptake (%)	550	570

10 It will be appreciated from the above that, contrary
to expectations, there does not appear to be any detriment
in dissolving the sulphonated polymer at a high
temperature (e.g. 150°C).

15 Examples 10b-f Sulphonation and subsequent dissolution of
Polymers from Examples 9b-f

The polymers from Examples 9b-f respectively were
sulphonated as described in Example 7, dissolved in NMP at
20 150°C, filtered through a 10 micron filter, cast on to
clean glass plates and drawn down, using a Gardner Knife.
The solvent was evaporated at 100°C under vacuum for 24
hours producing membranes of mean thickness of 40 microns.

The boiling water uptake was determined as described in Example 8a. The results are detailed in the Table below.

Sulphonated polymer from Example	Concentration in NMP (%w/w)	Boiling Water Uptake (%)	Theoretical EW	Measured EW (by titration)
10a	15	550	564	564
10b	10	190	559	564
10c	10	135	558	571
10d	10	109	557	591
10e	8	82	550	572
10f	15	520	583	602

5 Example 11a Comparison of Fuel Cell Performance of Example 10c, Example 10f and Nafion 115 (a commercially available material)

10 The membrane of Example 10c and 10f were pre-treated by boiling in 1M sulphuric acid, allowed to cool to room temperature followed by thorough washing with deionised water. Membrane Electrode Assemblies (MEA) were prepared using standard platinum loaded, Nafion® impregnated Gas Diffusion Electrodes (E-Tek, Elat 0.35mg Pt cm⁻²) hot
15 pressed onto the membrane. The active area being 11.8cm². The following operating conditions were followed:

Hydrogen Pressure 3Barg
Air Pressure 3Barg
20 Hydrogen Stoichiometry 1.5
Air Stoichiometry 3
Cell Temperature 60°C
Current Density 0.7Acm⁻²

The comparative voltages at current density of 0.8 A cm^{-2} for the unreinforced and reinforced membranes were 0.64 and 0.6V respectively and for Nafion 115, the voltage was 0.4V.

5

The MEA using the membrane from Example 10f was very fragile and required very careful handling, whereas the membrane from Example 10c was robust.

10 Example 11b Determination of the Crystallinity Index
values of Sulphonated Polymers from Examples 9c and 9f by
WAXS

15 Membranes of the sulphonated polymers from Examples 9c and 9f as prepared in Example 8a were examined by WAXS as described in the Example 8c.

20 The WAXS pattern of the membrane from Example 9f exhibited only broad amorphous scatter, whereas the patterns of the membranes from Examples 9c exhibited sharper, crystalline peaks in addition to amorphous bands.

The results are detailed in the Table below.

Sulphonated polymer from Example	Crystallinity Index (%)
9f	0
9c	6

25

Example 12 Blends with polyethersulphone

Sulphonated polymer from Example 5d and polyethersulphone were dissolved in N-methylpyrrolidone (NMP) at concentrations shown in the Table below. The homogeneous solutions were cast onto clean glass plates and then drawn down to give 400 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24 hours produced membranes of mean thickness 40 microns.

The boiling water uptake of these membranes was determined as described in Example 8b. The results are detailed in the Table below.

Sulphonated Polymer from Example 5d %w/w	polyethersulphone %w/w	Boiling Water Uptake (%)
15	0	102
14.25	0.75	125
13.5	1.5	105

Example 13 - Blend with polyethersulphone

The procedure of Example 12 was followed except that sulphonated polymer from Example 9d was used instead of that from Example 5d. Results for the boiling water uptake are detailed in the table below.

Sulphonated Polymer from 9d (%w/w)	Polyethersulphone (%w/w)	Boiling Water Uptake (%)
15	0	109
14.25	0.75	84
13.5	1.5	74
12.75	2.25	69
12.0	3.0	49

Example 14

5 A 250ml 3-necked, round-bottomed fitted with a stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (11.36g, 0.052mole), 4,4'-bis(4-chlorophenylsulphonyl)biphenyl (LCDC) (25.17g, 0.05mole), 4,4'-dihydroxybiphenyl (6.21g,
10 0.0333mole), 4,4'-dihydroxybenzophenone (14.28g, 0.0667mole), and diphenylsulphone (90g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a
15 nitrogen blanket, dried sodium carbonate (10.6g, 0.1 mole) and potassium carbonate (0.28g, 0.002 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 1 hour.

20 The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.18kNsm⁻².

Example 15

A 250ml 3-necked, round-bottomed fitted with a stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (11.02g, 0.0505mole), 4,4'-dichlorodiphenylsulphone (14.36g, 0.05mole), 4,4'-dihydroxybiphenyl (6.21g, 0.0333mole), 4,4'-dihydroxybenzophenone (14.28g, 0.0667mole), and diphenylsulphone (83g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (10.60g, 0.1 mole) and potassium carbonate (0.28g, 0.002 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 140 minutes.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.39 kNsm⁻².

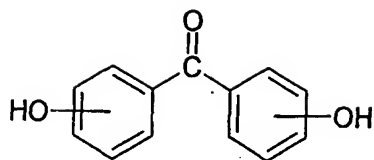
Example 16 Sulphonation of and subsequent dissolution and membrane fabrication of Polymers from Examples 14 and 15.

25

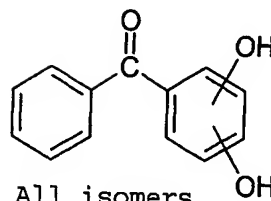
The polymers from Examples 14 and 15 were sulphonated as described in Example 7 and dissolved in NMP at 15 %w/w at 80°C and room temperature respectively. The homogeneous solutions were filtered through a 10 micron filter, cast on to clean glass plates and drawn down to give 400 micron films, using a Gardner Knife. The solvent was evaporated at 100°C under vacuum for 24 hours. The boiling water uptake was 39 and 108% for the sulphonated polymer from

Example 14 and 15 respectively, determined as described in Example 8b.

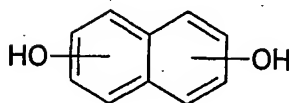
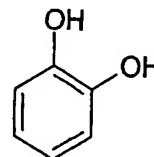
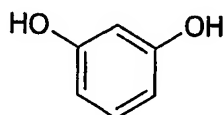
As an alternative to Bis-S, (or 2,4-DHB) other
5 moieties may be incorporated into the copolymer. Some
examples are as follows. It will be noted that all of the
examples shown are unsymmetrical about an imaginary line
which passes through the two -OH- groups. Whilst 4,4'-
dihydroxybenzophenone is unsymmetrical in the manner
10 described, the carbonyl moiety can be interchanged with an
ether moiety in a crystal structure so that polymeric
chains containing ketone and ether groups are
crystallisable. In contrast, an -SO₂- moiety cannot be
interchanged with an ether moiety so -SO₂- moieties act to
15 disrupt chains and reduce crystallinity.



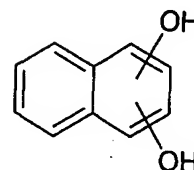
All isomers but not 4,4'-isomer



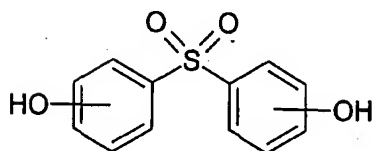
All isomers



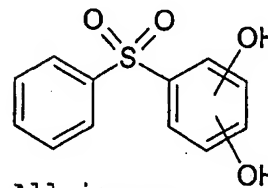
All isomers



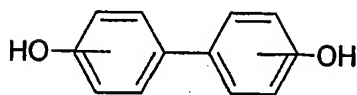
All isomers



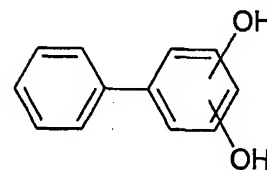
All isomers
- includes 4,4'-isomer



All isomers



All isomers but not 4,4'-isomer



All isomers

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

15

The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

25

30

CLAIMS

1. A polymer electrolyte membrane or a gas diffusion electrode which include a semi-crystalline copolymer
5 comprising:

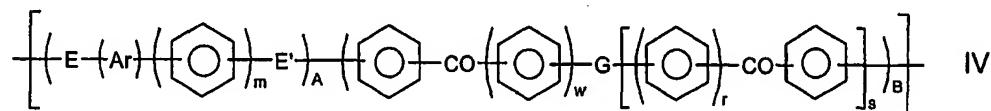
a first unit which includes an ion-exchange site;
a second crystalline unit; and
a third unit which is amorphous.
10
2. A polymer electrolyte membrane which includes a semi-crystalline copolymer comprising:

a first unit which includes an ion-exchange site;
15 a second crystalline unit; and
a third unit which is amorphous.
3. A membrane or electrode according to claim 1 or claim 2, wherein the level of crystallinity in said copolymer is
20 at least 0.5%.
4. A membrane or electrode according to any preceding claim, wherein said first unit is a repeat unit which includes aromatic group containing moieties linked by -
25 SO₂- and/or -CO- and/or -Q- groups, where Q is O or S.
5. A membrane or electrode according to any preceding claim, wherein said second unit is a repeat unit which includes aromatic group containing moieties linked by -CO-
30 and/or -Q- groups, where Q is O or S.
6. A membrane or electrode according to any preceding claim, wherein said third unit is a repeat unit which

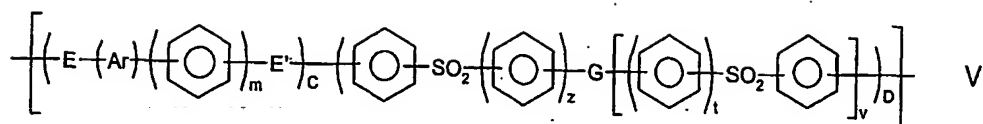
includes aromatic group containing moieties linked by -
 SO₂- and/or -CO- and/or -Q- groups, where Q is O or S
 provided, however, that said third unit suitably includes
 a means to render it amorphous (hereinafter said
 5 "amorphous means") and/or not crystallisable with
 polyarylether ketones or polyarylthioether ketones and/or
 not crystallisable with the second unit described above.

7. A membrane or electrode according to any preceding
 10 claim, wherein said third unit comprises a fourth unit
 which is of formula -Q-Z-Q- wherein Z represents said
 aromatic group containing moiety, wherein said fourth unit
 is not symmetrical about an imaginary line which passes
 through the two -Q- moieties provided, however, that said
 15 fourth unit is not derived from dihydroxybenzophenone
 substituted by groups Q at the 4- and 4'- positions.

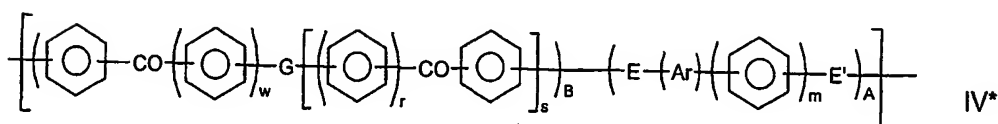
8. A membrane or electrode according to any preceding
 claim, wherein said copolymer includes a first unit which
 20 is of general formula



or of general formula

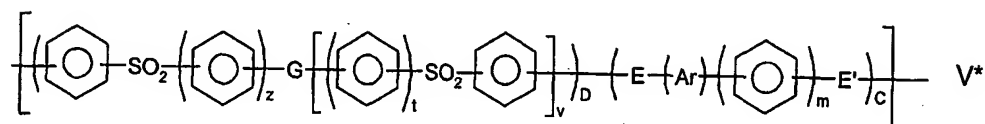


or of general formula



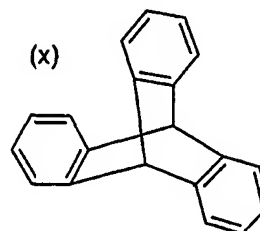
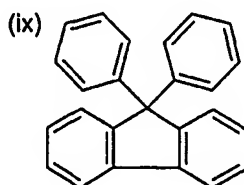
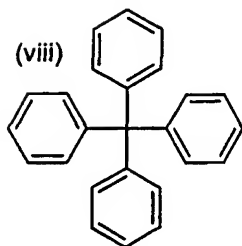
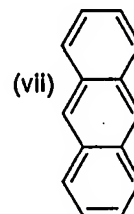
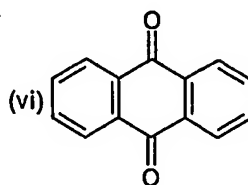
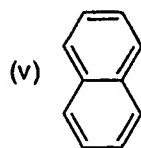
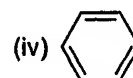
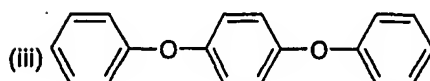
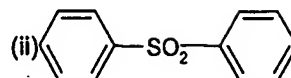
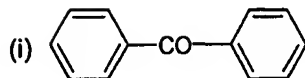
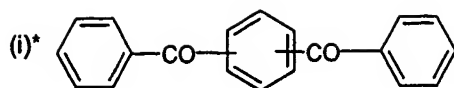
5

or of general formula



wherein said first unit is functionalised to provide ion-exchange sites; wherein the phenyl moieties in units IV, IV*, V and V* are independently optionally substituted wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)* and (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

20



9. A membrane or electrode according to any preceding claim, wherein said first unit is sulphonated to provide
5 said ion-exchange site.

10. A membrane or electrode according to any preceding claim, wherein said first unit includes a multi-phenylene moiety or fused ring aromatic moiety which is
10 , functionalised to provide said ion-exchange site.

11. A membrane or electrode according to any preceding claim, wherein said first unit includes a -O-biphenylene-O- or -O-naphthalene-O- moiety.

5

12. A membrane or electrode according to any preceding claim, wherein said second crystalline unit is of general formula IV or IV* as described in claim 8, provided said unit is crystalline.

10

13. A membrane or electrode according to any preceding claim, wherein said third unit is of general formula IV, IV*, V or V* provided said unit is amorphous.

15

14. A membrane or electrode according to any preceding claim, wherein said first unit is selected from -ether-phenyl-ketone-phenyl, -ether-phenyl-ketone-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl, -ether-biphenyl-ether-phenyl-ketone-phenyl, -ether-phenyl-ether-phenyl-ketone-phenyl, -ether-naphthalene-ether-phenyl-ketone-phenyl, -ether-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl, -ether-diphenyl-ether-phenyl-sulphone-phenyl, -ether-phenyl-ether-phenyl-sulphone-phenyl and ether-phenyl-sulphone-phenyl.

25

15. A membrane or electrode according to any preceding claim, wherein said second unit is selected from ether-phenyl-ketone-phenyl-ketone-phenyl-, ether-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl-, ether-phenyl-ether-phenyl-ketone-phenyl-, ether-phenyl-ketone-phenyl-, ether-phenyl-ketone-phenyl-, ether-phenyl-ketone-phenyl-ether-phenyl-ketone-phenyl-ketone-phenyl and ether-biphenyl-ether-phenyl-ketone-phenyl-.

30

16. A membrane or electrode according to any preceding claim, wherein said third unit is selected from ether-phenyl-sulphone-phenyl, ether-phenyl-ether-phenyl-sulphone-phenyl and a 1,3-dioxy-4-(phenylcarbonyl)phenyl moiety.

17. A device selected from a fuel cell, electrolyser or gas diffusion electrode, the device incorporating a semi-crystalline copolymer according to any preceding claim.

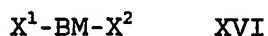
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18. A method of manufacturing a device selected from a fuel cell, electrolyser or gas diffusion electrode, the method including the step of using a semi-crystalline copolymer to prepare an ion-conducting element of the device.

15

19. A process for the preparation of a semi-crystalline copolymer as described in any of claims 1 to 16, the process comprising polycondensing a compound of formula

20



with a compound of formula

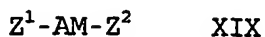


and with a compound of formula



30

and with a compound of formula



5 thereby to prepare a copolymer, wherein Y^1 represents a halogen atom or a group -EH (or -E'H if appropriate) and X^1 represents the other one of a halogen atom or group -EH (or -E'H if appropriate), Y^2 represents a halogen atom or a group -E'H and X^2 represents the other one of a halogen
10 atom or a group -E'H (or -EH if appropriate) and Z^1 and Z^2 represent a halogen atom or a group -EH (or E'H if appropriate);

and wherein BM represents part of a base monomer, SU
15 represents part of a moiety which is functionalised or can be functionalised (suitably independently of other moieties in the copolymer) to provide ion-exchange sites, XT represents a part of a crystalline or crystallisable moiety and AM represents part of an amorphous moiety.

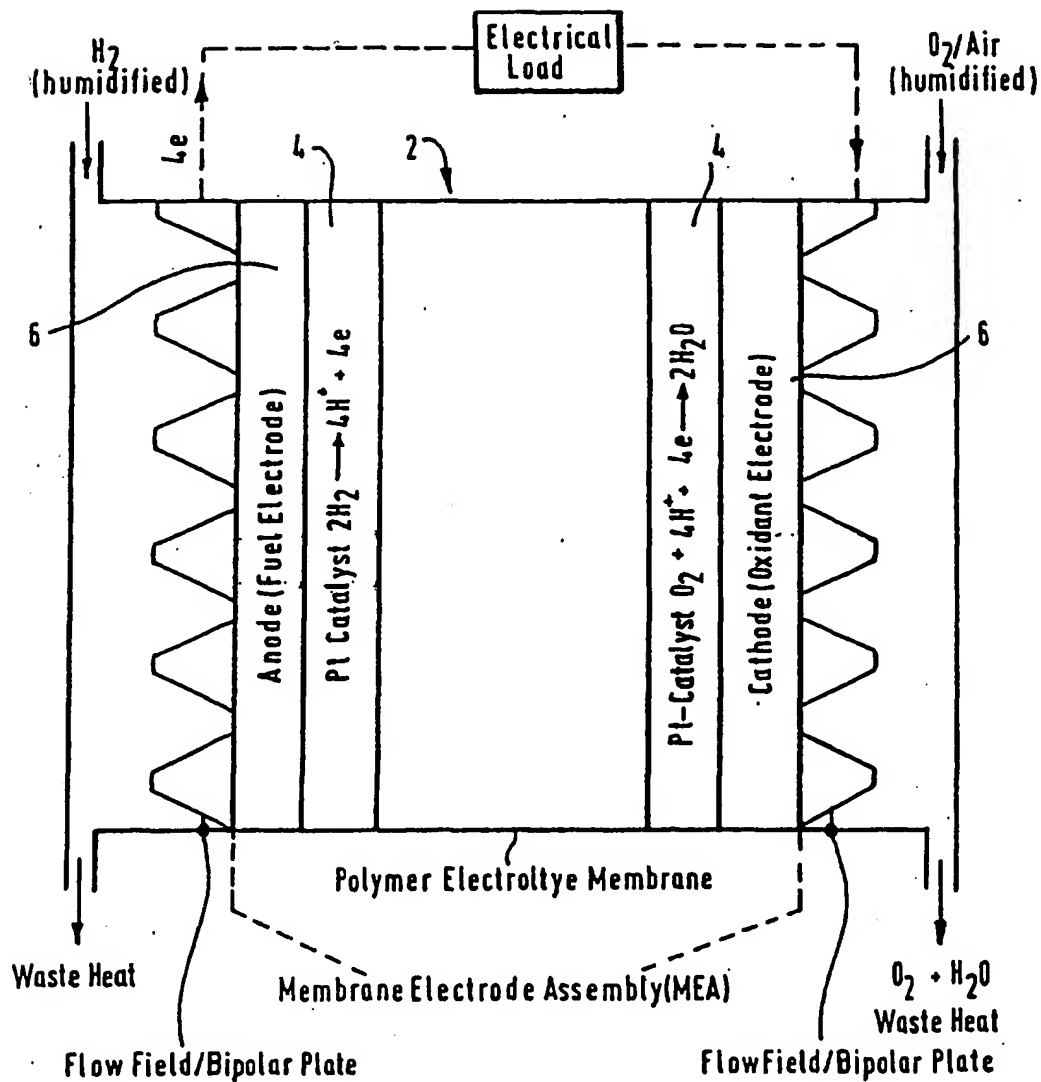


Figure 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/01232

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 7	C08J5/22	H01M8/10 H01M4/86 H01M2/16 C08G65/48 H01M10/40
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01M C08G C08J H01B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 15691 A (CHARNOCK PETER ; VICTREX MFG LTD (GB); WILSON BRIAN (GB); KEMMISH D) 23 March 2000 (2000-03-23) page 2, line 31 -page 5, line 4 page 6, line 30 -page 7, line 4 page 8, line 1 -page 9, line 11 page 11, line 15 -page 18, line 13 page 19, line 19 - line 30 page 20, line 8 - line 28 page 21, line 29 - line 33 page 23, line 1 - line 4 claims 1-35; examples 1-26 --- -/--	1-19
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *Z* document member of the same patent family		
Date of the actual completion of the international search 19 September 2001		Date of mailing of the international search report 27/09/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Gamez, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/01232

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,L	WO 01 19896 A (BRIDGES RICHARD FRANK ;CHARNOCK PETER (GB); VICTREX MFG LTD (GB);) 22 March 2001 (2001-03-22) "I" so quoted as doubt on the priority validity page 2, line 9 -page 5, line 9 page 7, line 7 - line 14 page 8, line 10 -page 13, line 18 page 16, line 23 -page 21, line 20 page 25, line 30 -page 29, line 10 page 33, line 1 -page 37, line 14 claims 1-25; examples 1-12 ---	1-19
A	WO 95 15991 A (HYDRO QUEBEC ;MASSON JACQUELINE (FR); SANCHEZ JEAN YVES (FR); ALLO) 15 June 1995 (1995-06-15) page 3, line 10 - line 36 page 9, line 10 - line 16 page 10, line 9 - line 13 claim 1; examples 1-5 ---	1-3
A	US 4 657 990 A (DAOUST DANIEL J M ET AL) 14 April 1987 (1987-04-14) column 1, line 31 - line 38 column 1, line 62 -column 2, line 15 column 3, line 12 - line 47 column 4, line 35 - line 50 column 7, line 58 -column 8, line 25 examples 1-21 ---	1-5, 7-10, 14-19
A	EP 0 574 791 A (HOECHST AG) 22 December 1993 (1993-12-22) page 3, line 41 -page 4, line 11 page 8, line 46 -page 11, line 34 -----	1,4-6, 8-10, 14-18

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-19 relate to an extremely large number of possible membranes, electrodes, devices, methods and processes : support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of thereof. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the use of polyarylether ketones or polyaryether sulphones described in the examples of the present application in membranes, electrodes, devices, methods and processes.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/01232

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0015691	A	23-03-2000	AU 5750999 A EP 1112301 A1 WO 0015691 A1	03-04-2000 04-07-2001 23-03-2000
WO 0119896	A	22-03-2001	AU 7025000 A WO 0119896 A1	17-04-2001 22-03-2001
WO 9515991	A	15-06-1995	FR 2713646 A1 CA 2155567 A1 DE 69426291 D1 DE 69426291 T2 EP 0683801 A1 WO 9515991 A1 JP 8507827 T US 5700880 A	16-06-1995 15-06-1995 21-12-2000 23-05-2001 29-11-1995 15-06-1995 20-08-1996 23-12-1997
US 4657990	A	14-04-1987	AT 42961 T DE 3570085 D1 EP 0152161 A1 ES 539694 D0 ES 8606441 A1 JP 60163926 A	15-05-1989 15-06-1989 21-08-1985 16-04-1986 01-10-1986 26-08-1985
EP 0574791	A	22-12-1993	CA 2098238 A1 DE 59309908 D1 EP 0574791 A2 JP 6093114 A SG 73410 A1 US 5438082 A US 5741408 A US 5561202 A US 6214488 B1	14-12-1993 27-01-2000 22-12-1993 05-04-1994 20-06-2000 01-08-1995 21-04-1998 01-10-1996 10-04-2001

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